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NANOSTRUCTURED CARBON COATINGS

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Abstract

This paper provides an overview of nanocrystalline and nanostructured carbon coatings and explores a very broad range of potentially important carbon nanostructures that may be used in future technologies. A new method for the synthesis of nanostructured carbon coatings on the surface of SiC and other metal carbides is described. This method is accomplished through the extraction of metals from carbides by supercritical water or halogens in a high temperature reactor.

This is a versatile technology because a variety of carbon structures can be obtained on the surface of carbides in the same reactor. Not only simple shapes or fibers, but also powders, whiskers and components with complex shapes and surface morphologies can be coated. This technology allows for the control of coating growth on the atomic level, monolayer by monolayer, with high accuracy and controlled structures.

Ordered and disordered graphite, nanoporous carbon (specific surface area of 1000 m²/g and more) and hard carbon can be formed depending on the temperature and gas composition. These carbon coatings can be used as tribological coatings having a low-friction coefficient for a variety of applications, from heavy-load bearings to nanocoatings for MEMS; protective coating for sensors and tools, intermediate thin films for further CVD deposition of diamond, weak coatings on SiC reinforcements for composite materials, coatings on SiC powders for improved sinterability, catalyst supports, molecular membranes for sensors, etc. The structure and properties of carbon coatings obtained on the surface of SiC have been investigated using an array of analytical techniques.

1. Introduction

Nanotechnology has been recognized as an emerging technology of the next century [1]. Control over the structure of materials on nanoscale can open opportunities for the development of nanocrystalline materials with controlled properties, if the structure/property relations are known. The coating industry is a major industry worldwide. Coatings are needed to prevent wear, erosion and corrosion, to provide

electrical or thermal insulation, to act as selective membranes, etc. There is a need for coatings with improved performance [2]. Typically, materials with the structural elements ranging from 1 to 100 nm are considered to be nanocrystalline. Such structural features are smaller by factors of 10 to 1000 compared to microcrystalline materials. This can offer potential for significant improvements or modification of certain properties, since most of them are controlled by the structural features of materials.

Carbon is among the most important and widely used materials in all areas: chemistry (catalyst support, absorbent), electrochemistry (electrodes), bioengineering (biocompatible implants), mechanical engineering (C/C composites), tribology (solid lubricant), metallurgy (crucibles and heaters), glass industry (mold coating), electronics (substrates) and in many other fields. In some of these applications, carbon coatings are as important as bulk materials, and sometimes only thin coatings can be used. For instance, carbon layers with a high specific surface area are important in catalysis and hard diamond-like modifications are useful for wear resistant parts [3, 4] as coatings with an adjustable hardness. Carbon coatings have a variety of structures, with diamond and graphite being the main industrial products. However, new carbons are challenging the traditional materials and an enormous growth of applications and manufacturing techniques have emerged in this area during the past decade. Some of them will be analyzed in this paper.

Novel carbon materials, including nanostructured films, are manufactured under severe control for purity, structure and texture to achieve the ultimate properties or give them new functions. In Japan, a New Carbon Forum was established in 1988 to coordinate all activities in the area of novel carbon materials. It consists of representatives of leading Japanese companies and selected academics, and contributes significantly to the growth of this area and in attracting increasingly significant funding. A new term Carbon Alloys [5] was introduced by Japanese scientists in 1992 to describe the variety of carbon materials, including ones containing additives of other elements. In most countries, including the US, activities in the areas of traditional carbons (graphite), diamond and fullerenes/nanotubes are separated and scientists working in these areas belong to different professional societies and rarely meet at the same conference. As a result, according to the recent assessment of R&D status and trends in nanoparticles [1], Japan is leading in the area of carbon-based nanoparticles for coating and devices, followed by Europe and then the US. This paper attempts to provide a short crosscutting overview through all areas and all kinds of nanocrystalline carbon films, both high-tech, such as nanocrystalline diamond, and low-tech, such as soot.

It is important to distinguish between "nanocrystalline" and "nanostructured" materials. Carbon is intrinsically a nanocrystalline material. Most industrial carbons, except diamond crystals, well-ordered graphite and amorphous coatings, are nanocrystalline. For example, common carbon black has a particle size of about 30 nm. Moreover, it is much easier to produce nanocrystalline carbon than a well-crystallized one. Scientists traditionally worked on obtaining large crystals, particularly in the case of diamond, to achieve the ultimate properties. Thus, the size of crystals in the nano range does not bring an advantage by itself. However, it can be advantageous in the case of the use of nanotechnology to tailor the nanostructure to satisfy property requirements.

2. Review of Nanostructured Carbon Coatings

2.1. NANOPOROUS FILMS AND HIGH SURFACE AREA MATERIALS

High surface area ($300\text{--}2000\text{ m}^2/\text{g}$) materials are used in applications that require rapid and responsive sampling, selective separation, and catalytic processing. The growing area of chemical sensors requires new nanostructured materials, particularly thin films.

Nanoporous carbons, also often referred to as carbon molecular sieves, can be considered amorphous, that is, they have no long-range order. However, they display a remarkable regularity in the distribution of pore dimensions, having a pore size of about 0.5 nm [6]. These carbons have a requisite pore diameter to provide shape selective effects in the transport and adsorption of small molecules. TEM shows that these carbons contain "wormlike" structures. The combination of short persistence length and regions of high curvature gives rise to incoherence and structural complexity [6]. Hence, the materials are simultaneously regular (on the nanoscale and below) and x-ray amorphous. Thus, calling such carbon films amorphous is not strictly appropriate, given the regularity of structure.

2.2. FULLERENES

Fullerene films can be prepared by vacuum deposition on a variety of substrates [7]. Photoinduced polymerization of solid fullerene films can increase their stability to organic solvents such as boiling toluene [8]. Our recent work demonstrated the stability of fullerenes in supercritical water at temperatures of up to 500°C [9]. However, applications for these films are still to be found.

Onion-like carbon particles [10], which can be considered as giant fullerenes or their relatives, are not produced in large quantities and it is not clear what benefits can be achieved by using them. Further research into both, synthesis and property characterization of these carbon structures is required.

2.3. NANOTUBES AND NANOFIBERS

Single- and multiwall nanotubes represent the small-size part of this group, while graphite filaments can have diameters ranging from a few nm to hundreds of nm. Although these fibrous materials cannot be considered as a typical coating, they can be grown as a layer on a substrate (Fig. 1a) and find use in sensors, catalyst supports, etc. Moreover, carbon nanotubes are primarily grown on a substrate in fixed-bed reactors [11].

The structure of the graphite filaments can be varied from a cylindrical hollow-cored to ribbon like with stacking of graphite layers perpendicular to the ribbon surface [12]. Fishbone structure of nanotubes has been also reported [11]. Graphite nanofibers consisting of graphite platelets $3\text{--}50\text{ nm}$ in width are capable of sorbing and retaining in excess of 20 l/gram of hydrogen when exposed to the gas pressures of 120 atm at room temperature [13]. Carbon filaments with periodic conical internal voids (Fig. 1b,c) have been produced by decomposition of paraformaldehyde under hydrothermal conditions at

700-750°C under 100 MPa [14]. Application of nanotubes and nanofibers as catalyst support is currently considered [11].

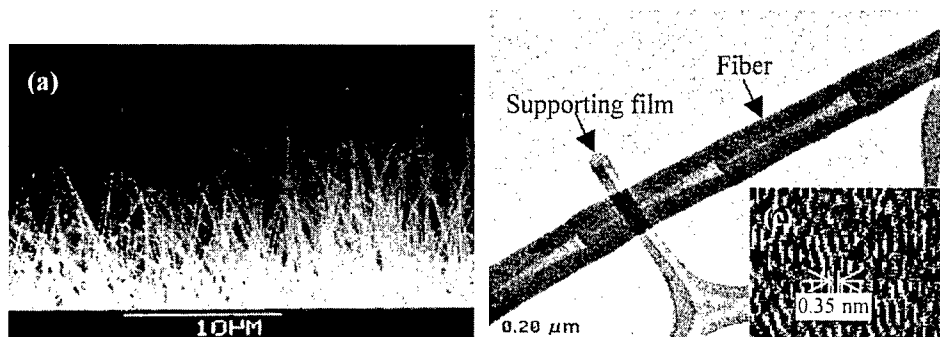


Figure 1. SEM (a) and TEM (b,c) micrographs of carbon fibers (about 200 nm thick) grown on a substrate by hydrothermal decomposition of paraformaldehyde [14].

2.4. NANOCRYSTALLINE DIAMOND AND DLC FILMS

Nanocrystalline diamond films can provide very smooth coatings having high hardness and other properties of polycrystalline diamond films, and a very low friction coefficient of 0.1 or less [3].

As is shown in the work conducted at Argonne National Laboratory [15, 16] nanocrystalline diamond can be obtained from C_{60} by chemical vapor deposition (CVD). The deposition mechanism proposed is through the carbon dimer, C_2 , which forms by microwave fragmentation of vapor phase C_{60} followed by growth on a heated silicon substrate. There is no incorporation of hydrogen into these nanocrystalline diamond films. This is due to the fact that it is not present in the growth environment or present in only very small quantities. High growth rates are attributed to the mechanism of direct incorporation of the C_2 species into a hydrogen-free diamond lattice, which is in contrast to the mechanism of growth by adsorption of CH_3 radicals which requires subsequent desorption of the hydrogen as a step in the process. The films produced in this process are nanocrystalline for which nucleation rates of $\sim 10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$ are indicated to account for the microstructure. The direct insertion of C_2 dimers into (100) faces is supported by theoretical calculations [17] which also provide an explanation for the absence of a graphitic phase in this process.

The instantaneous transformation of C_{60} to bulk polycrystalline diamond under rapid nonhydrostatic compression has been reported [18]. A sample of C_{60} held in a graphite capsule was compressed in a diamond anvil with slightly non-parallel faces which applied a pressure gradient while compressing the sample to 20 GPa. The application of a pressure gradient results in non-hydrostatic stress on C_{60} molecules which collapse and undergo a phase transformation into diamond. Thin ($\sim 5 \mu\text{m}$) and transparent nanocrystalline diamond films can also be obtained by shock compression of fullerene films [7]. With the fall in cost of fullerene powders, this method may become important in the future as a method to produce nanocrystalline diamond free of metal impurities.

Diamondlike carbon (DLC) films are often considered to be amorphous. These films can be deposited at lower temperatures compared to diamond. Recent work shows that if electron cyclotron resonance plasma is used, DLC films obtained at room temperature can contain nanocrystalline cubic or hexagonal diamond [19]. Amorphous DLC (a-C:H) films can be crystallized by laser treatment producing a mixture of diamond nanocrystals of 2-7 nm in size and graphite particles of 2-4 nm in size. Thus, amorphous carbon films can be nanostructured through the control of manufacturing or post-growth modification.

2.5. CARBON-BASED NANOCOMPOSITES

2.5.1. *Diamond-like Nanocomposites*

DLC coatings modified by Si and other metals are produced under the commercial name Dylyn[®] by Advanced Refractory Technologies [20] and are marketed in the US and worldwide. Their mechanical, electrical and optical properties can be tuned over a wide range by changing deposition conditions and composition, such as doping with metals. This kind of coating is a good example of property control achieved by material modification on the nanolevel. In particular, they have a low friction coefficient of 0.05-0.2 and excellent wear resistance.

2.5.2. *Silicon-containing Composites*

Up to 11% Si can be nanodispersed in CVD carbon [21]. Small clusters of a few silicon atoms are located in regions of disordered carbon, which separate small regions of organized graphene layers. This material is promising for electrode applications, particularly in advanced lithium batteries.

It is necessary to mention that most of silicon carbide materials made from polymeric precursors (Tyranno[®], Blackglas[®], Nicalon[®] and other) are in fact SiC-C-SiO_x composites. Interlayers of carbon determine many properties of these important materials. Many of them are used for manufacturing protective coatings. The attractive prospect of polymer decomposition to carbon-based composites is that the polymer can first be applied in thin films and then would be transformed to carbon by laser or thermal pyrolysis.

2.5.3. *Encapsulated Metals and Carbides*

Synthesis of nanometer-size single crystals encapsulated in carbon cages or nanotubes has been achieved [22]. Those crystal particles are primarily carbides (WC, TaC, YC₂, SiC [23] and other) and metals (Fe, Ni, Co, [24], and Pd [25]). Carbon encapsulation can help to prevent interaction of nanoparticles with the environment, accelerate sintering of carbides, or prevent grain growth during sintering. Magnetic metal or carbide particles are of interest for potential applications in which iron oxide particles are currently used: in magnetic data storage, for magnetic toner in xerography, in ferrofluids and as contrast agents in magnetic resonance imaging [26]. Several metal particles can be encapsulated in continuous carbon structures known as carbon socks [27] or in multiwall carbon nanotubes. Typically, the particles are covered by a few well-ordered layers of graphitic carbon.

2.6. CONVENTIONAL NANOCRYSTALLINE CARBON COATINGS

Not only high-tech carbons are nanocrystalline. There exists a large market for conventional nanocrystalline carbon coatings for a variety of applications. Fig. 2 shows a typical soot coating which can be produced by combustion of acetylene in oxygen-lean flames [28]. The average particle size is 30-50 nm. The structure of the coating can

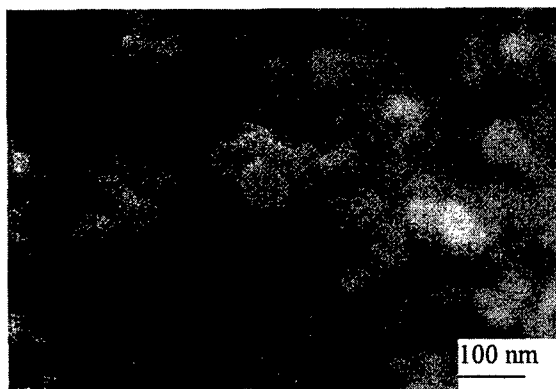


Figure 2. Field emission scanning electron micrograph (FESEM) of a soot coating produced using acetylene flame.

be controlled by changing the acetylene/oxygen ratio and flame temperature. Acetylene/oxygen ratio of about 1:1 would result in the formation of diamond if the substrate is properly cooled [29]. Polycrystalline diamond films may be grown at the rate of tens of microns per hour at atmospheric pressure. It was found that the morphology of the deposit depended on the substrate temperature and gas. Thus, flame synthesis of carbon coatings allows for control over the arrangement of carbon atoms and can produce a variety of structures from graphitic carbon to diamond.

2.7. ANALYSIS OF NANOSTRUCTURED CARBON

Advanced analytical techniques must be used to study all nanocrystalline materials. However, the analysis of carbon requires considerable care and caution due to the variety of existing carbon allotropes. Analysis of nanocrystalline carbons by X-ray diffraction is usually inconclusive because many nanostructured carbons are X-ray amorphous. For this purpose electron microscopy, especially TEM combined with SAD and EELS is useful, but it is a slow and expensive method. FESEM is more valuable to examine the growth habit of larger structures (> 10 nm). AFM can be a valuable tool for surface studies as well.

Investigators generally apply Raman spectroscopy to study carbons due to its speed and simplicity of use. Diamond gives a sharp peak at 1332 cm^{-1} [30], which is shifted to lower wavenumbers and accompanied by a band at about 1140 cm^{-1} in the nanocrystalline state [31]. Nanocrystalline graphite gives bands at $\sim 1580\text{ cm}^{-1}$ (G-band) and $\sim 1355\text{ cm}^{-1}$ (D-band). The D-band is reported to occur over the range $1343\text{--}1360$ using the 514 nm wavelength excitation [32] depending on the degree of disorder and/or stress. The G-band at 1582 cm^{-1} appears to shift up with increasing disorder. The degree of graphitization has been correlated to the ratio of intensities of the G and D-bands [33], where in highly amorphous carbon, the D-band is stronger than the G-band. Recent analysis of graphitic carbons has explored the linear dependence of the D-band on the laser excitation energy [34]. Conventional visible wavelength Raman

spectroscopy fails to determine nanocrystalline diamond when it is mixed with graphite. In this case, UV excitation Raman spectroscopy can provide greater sensitivity [35].

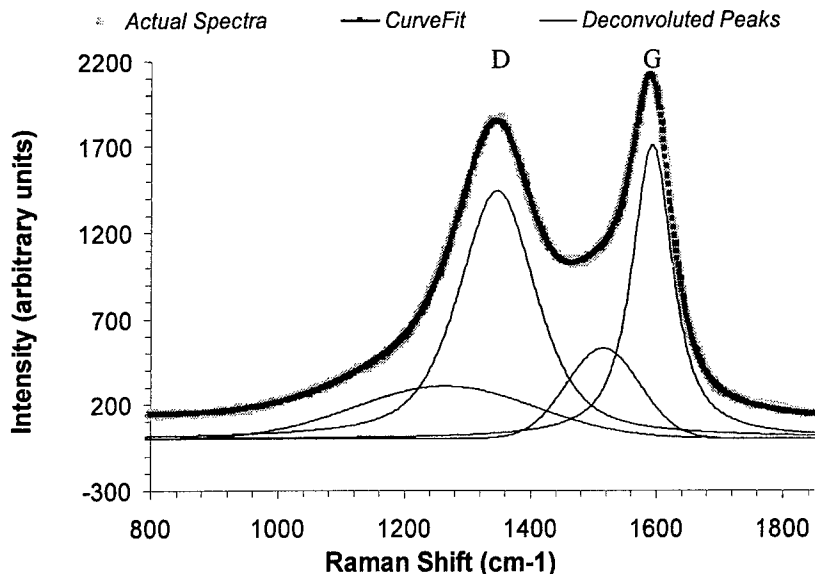


Figure 3. Deconvoluted Raman spectra for a sintered SiC specimen treated in 3.5% Cl_2 -Ar for 5 hours at 1000°C [36].

A typical spectrum of nanocrystalline carbon in Fig. 3 shows characteristic D (1343 cm^{-1}) and G (1600 cm^{-1}) bands for graphite, however, detailed examination of the spectrum shows that its shape cannot be accurately matched by these two bands alone. Better agreement was achieved when the spectrum was deconvoluted with the addition of two broad bands centered at 1225 cm^{-1} and 1500 cm^{-1} . These bands are associated with disorder in carbon, and are consistent with nanocrystalline or amorphous graphite or with sp^3 bonding which would provide improved hardness, exceeding that of SiC, to the carbon layer [36].

Fullerenes [9] and single wall carbon nanotubes [37] have characteristic Raman spectra with multiple bands, while Raman spectra of multiwall nanotubes are similar to that of nanocrystalline graphitic carbon.

3. Synthesis of Carbon Coatings by Selective Leaching of Carbides

Many carbon coatings are applied to the surface of carbides. Carbide ceramics such as SiC, B_4C , WC and TiC have good wear resistance and find a number of applications because of their high hardness. However, their dry friction coefficient is about 0.6-0.7. Better tribological performance can be expected if the ceramic is coated with a carbon film to reduce the friction coefficient. Tungsten carbide tools are often coated with diamond films to reduce the wear. Mechanical and chemical stability are also limiting

factors for high surface area materials and new methods of synthesis can help to overcome this problem.

In particular, the nanostructured carbon coatings obtained on the surface of silicon carbide can be used for the following purposes:

- Diamond coatings would be important in SiC electronic devices, as protective coating for sensors and tools, for "diamondization" of SiC powders for abrasive applications, and intermediate thin films for further CVD deposition of diamond.
- Ordered and disordered graphitic carbon coatings can be used on SiC reinforcements for composite materials (fibers, whiskers, platelets), as tribological coatings for a variety of applications (e.g., seals), and coatings on SiC powders for improved sinterability.
- Nanoporous carbon coatings (specific surface area of 1000 m²/g and more) can be used as catalyst supports, molecular membranes for sensors, or interlayers for the micro-joining of SiC components to Si wafers through reacting carbon with Si.
- Hydrogenated (a-C:H) and diamond-like carbon films have potential as tribological coatings having a low-friction coefficient for a variety of applications, from heavy-load bearings to nanocoatings for MEMS.

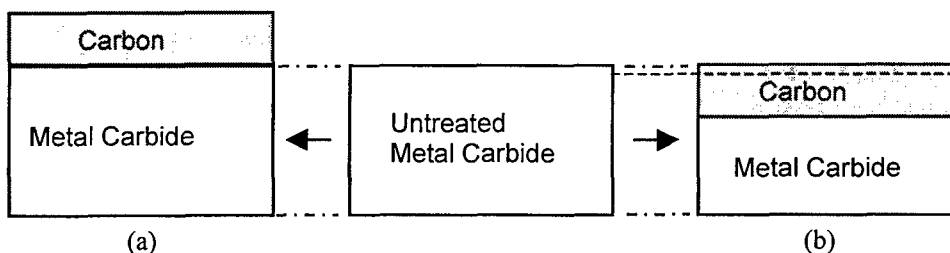


Figure 4. Carbon coating via vapor deposition (a) and selective leaching of carbides (b).

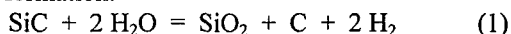
CVD or physical vapor deposition PVD are used to obtain a variety of carbon coatings ranging from diamond to graphite and amorphous carbon. However, adhesion of vapor deposited coatings is always a problem. Additionally, the size of the coated component increases (Fig. 4a) which is not always desirable, especially when these objects are thin, e.g., SiC fibers or MEMS devices. There is no current technology allowing to produce uniform carbon coatings within pores in a porous ceramic body, or on whiskers/platelets/fiber preforms without bridging the particles/fibers. Thus, the search for new methods of producing nanostructured carbon coatings continues.

Since carbides contain carbon in their structure, it is possible to produce a carbon coating by leaching the metal and leaving carbon layer behind. Such coating is not deposited onto the surface, rather the surface is transformed into carbon (Fig. 4b). As a result, the thickness of the coated component does not increase. It remains the same or decreases slightly. The structure and composition of the coating can be controlled with high precision, leaching metal layer by layer. This technique is particularly good for nanostructured coatings. We suggested this method 5 years ago, using supercritical

water for leaching [38], and later expanded it for the use of halogens [39]. A brief overview of the structure of nanocrystalline coatings produced by leaching carbides will be given in the following sections.

3.1. HYDROTHERMAL SYNTHESIS

Hydrothermal leaching of silicon carbide has been studied in detail [38], [40-44]. In these experiments, SiC samples were placed in capsules with distilled water and treated at temperatures of 300-850°C and pressures of 10-500 MPa. The following reaction was predicted by thermodynamic calculations [45] for the Si-C-H-O system to lead to solid carbon formation:



This reaction is thermodynamically favored at relatively low water/carbon ratios. The critical factor here is that as soon as silica is formed, it dissolves in the fluid. Thus, the reaction (1) tends to move further to the right, leading to the growth of the carbon coating.

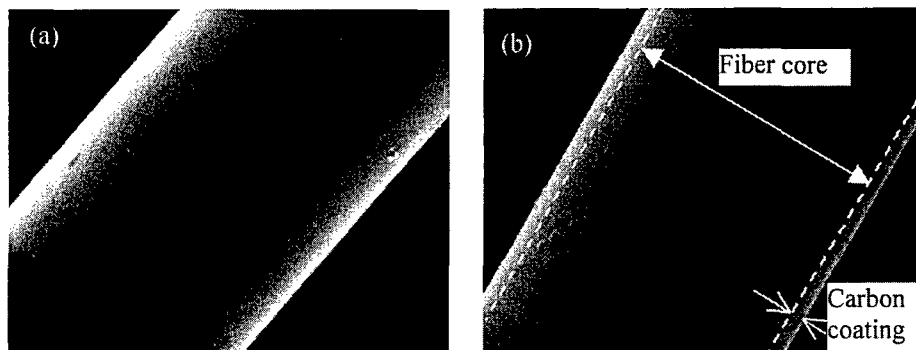
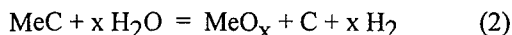


Figure 5. Typical SEM micrographs of a desized Tyranno® SiC fiber (a) and a fiber after hydrothermal treatment at 400°C. The fiber shown in (b) has a carbon coating of about 500 nm, but the surface roughness did not change after treatment. Fiber diameter is 11 μm .

Carbon formation during hydrothermal leaching of SiC demonstrates that the hydrothermal method can be useful for producing carbon coatings. In particular, we used this approach to obtain carbon coatings on SiC fibers (Fig. 5) and particles [43]. Carbon films on SiC fibers with thickness of 10 nm to 1 μm were obtained and used for interfacial engineering in ceramic matrix composites, to ensure fiber pull-out and graceful fracture of composites [46]. The treatment temperature can be reduced from 350-400°C to 250°C by using alkaline solutions instead of pure water [47]. The carbon layer produced is very smooth and uniform (Fig. 5b). AFM study [48] showed that the surface topology of the fiber remains unchanged after leaching. This is possible because the size of graphite crystallites, according to Raman spectroscopy analysis, does not exceed 5 nm and is typically about 2 nm. Thus, removal of Si as $\text{Si}(\text{OH})_4$ or similar species at low temperatures does not cause collapse of crystals producing a nanoporous films similar to those described in Section 2.1. A similar shape retention was observed

for SiC powders, even when those were completely transformed to carbon [23]. TEM analysis showed that SiC powders can be coated with 3-4 monolayers of graphite providing carbon encapsulation [23] described in Section 2.5.3.

This method can potentially be applied to other carbides as well [45]. The reaction (1) can be written in the general form for hydrothermal leaching of carbides with the formation of carbon as following:



The use of large-volume autoclaves instead of small pressure vessels that were used in our experiments can make this method attractive for industrial use. However, the hydrothermal method can only be applied to the carbides that form soluble or volatile hydroxides, e.g., $\text{Si}(\text{OH})_4$. This limits the range of materials to be coated. Thermodynamic analysis [39] predicts that the extraction of metals from carbides by halogens (e.g., Cl_2) or their compounds (e.g., HCl) can also lead to the formation of free carbon. This method can be used to obtain carbon coatings on TiC and other carbides that form volatile halides, but do not form soluble or volatile oxides.

3.2. LEACHING BY HALOGENS

Carbon films can be produced on SiC surfaces by high temperature chlorination because SiCl_4 is more thermodynamically stable than CCl_4 at elevated temperatures, so that chlorine reacts selectively with the Si at SiC surfaces according to the reactions:



leaving carbon behind. The structure of the carbon layer is affected by temperature and the composition of the chlorinating gas mixture. Carbon films have been produced on β -SiC powders [39] as well as SiC based fibers [46] and monolithic CVD and sintered ceramics [49] exposed to $\text{Ar-H}_2\text{-Cl}_2$ gas mixtures at atmospheric pressure at temperatures between 600 and 1000°C.

After a treatment of β -SiC in 3.5% Cl_2 at 600°C (Fig. 6a), the XRD pattern was similar to that of as-received powder. After reacting with 3.5% Cl_2 -Ar at 800°C and 1000°C (Fig. 6b) the intensity of β -SiC reflections diminished and they disappeared with increasing reaction time. However, no other peaks were detected. Only long-term treatment of bulk ceramics resulted in some well-crystallized graphite that could be detected by XRD.

In the Raman spectra of the powders treated in 3.5 % Cl_2 at 600°C and 1000°C, bands of disordered graphite were observed (Fig. 3). The average size of graphite crystallites formed in the treatment with 3.5% Cl_2 was estimated as 2-4 nm (Table 1) using the Tuinstra-Koenig equation [33].

The TEM micrographs show that as the temperature increases, thicker and better ordered carbon films grow due to the reaction with Cl_2 atmosphere (Fig. 6b). These films produce electron diffraction patterns of graphite.

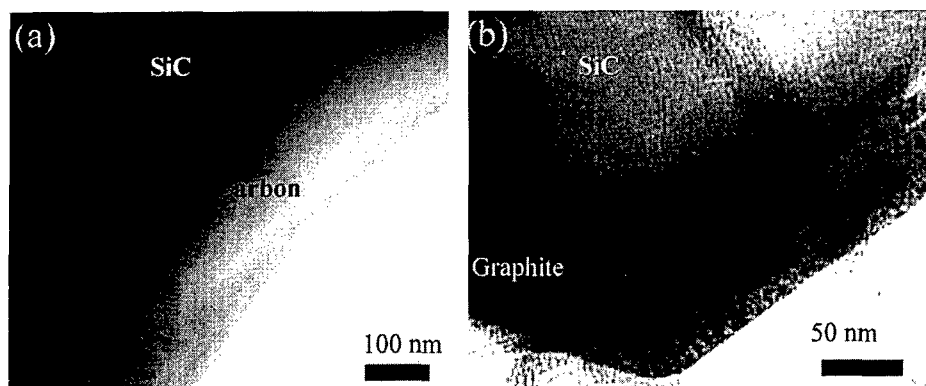


Figure 6. Bright field TEM micrographs showing an amorphous carbon film on β -SiC after treatment in Ar/3.5%Cl₂ at 600°C for 27 hrs (a) and a graphitic film after treatment at 1000°C for 72 h (b) [39].

TABLE 1. Surface area and size of graphite crystallites in SiC powders treated in Ar/Cl₂ and Cl₂/H₂ gases [39].

Experimental conditions			BET measured specific surface of powder (m ² /g)	Carbon content (%)	Calculated surface area of carbon (m ² /g)	L _a (nm)
Gas	Temp. (°C)	Time (hrs)				
3.5% Cl ₂ /Ar	600	27	48	8	400	2.0 - 2.5
3.5% Cl ₂ /Ar	600	48	140	11	1163	2.4 - 2.6
3.5%Cl ₂ /Ar	1000	20	990	98	1010	2.0 - 4.5
2%Cl ₂ /2%H ₂ /Ar	1000	72	12	< 5	10	1.0 - 4.5
As-received β -SiC			13	< 3		2.0

It can be seen in Table 1 that the powder treated at 1000°C in Cl₂ has a specific surface area in excess of 1000 m²/g. This value is typical for nanoporous carbons (Section 2.1). Other experiments with Cl₂ produced powders with the surface area of 100-200 m²/g. However, these powders contained various amounts of non-reacted SiC. To determine the carbon content in the powders, the samples treated with the Cl₂ gas were oxidized in air in a temperature range from room temperature to 750°C and the weight changes were measured by TGA [39]. We found that all porous carbon coatings on SiC particles have a high surface area, but the surface area increases with increasing time and/or temperature of the treatment in Cl₂ (Table 1), probably due to slow etching of carbon.

Carbon films have also been formed on the surfaces of commercially available monolithic SiC specimens by high temperature chlorination at atmospheric pressure in Ar-Cl₂ and Ar-H₂-Cl₂ gas mixtures [49]. The carbon film forms in two layers, with the outer layer being a loosely adherent, coarse graphitic carbon. The lower layer, which is strongly adherent to the SiC, is nanocrystalline and hard. Raman spectroscopy and X-ray diffraction identified it as highly disordered carbon with characteristics of nanocrystalline graphite. Pin-on-disk tribology testing using a spherical silicon nitride

indenter showed that the presence of this layer reduced the friction coefficient by a factor of approximately six and the wear rate by more than an order of magnitude [36].

The kinetics of the growth of the dense carbon layer on SiC at 1000°C was found to be linear with time up to thickness in excess of 50 μm . This suggests the chemical reaction controlled process and not a diffusion controlled one [49]. Thus, the carbon film allows penetration of CCl_4 molecules through the layer as thick as 50 μm and is expected to be a nanoporous film. However, since the size of the SiCl_4 molecule is smaller than that of a hydrated silica molecule penetrating through the carbon layer in the case of hydrothermal leaching, the carbon film is expected to have a smaller pore size and hence, higher mechanical strength. Again, TiC and other carbides can be coated as thermodynamic modeling and preliminary experiments show [50].

3.3. DISCUSSION

We summarized typical carbon nanostructures that we observed in leaching experiments in Fig. 7. Although we observed all these structures in our experiments, this paper does not give us enough space to explain why and how this variety of carbon structure is formed. Reactions (1-4) lead to the formation of free carbon, that may maintain the sp^3 -structure which it has in carbide and form diamond. Alternatively, it can be transformed to the graphite, which is thermodynamically stable under these pressures or form various amorphous or disordered structures intermediate to diamond and graphite. By changing the experimental conditions, it is possible to tune the structure of the coating. For example, high temperatures will favor the formation of graphite, while amorphous coatings will be formed at low temperatures, when surface reconstruction is slow. Presence of hydrogen in the environment will stabilize sp^3 bonding leading to the formation of diamond or DLC [39, 51].

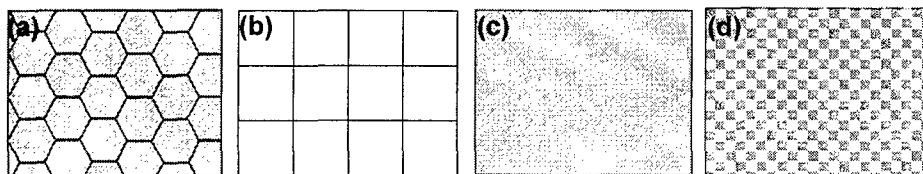


Figure 7. Schematic presentation of structures of carbon films that can be produced by leaching carbides. a - graphite, b - diamond or hard carbon, c - uniform amorphous carbon, d - nanoporous films with controlled pore size and surface area.

If the carbon atoms stay on their sites after metal is extracted from the lattice, one-dimensional growth of a porous carbon structure with a pore size comparable to the lattice parameter of the carbide substrate or molecules of the gaseous species that escape from the reaction interface. Thus, by changing the carbide we change the distance between the carbon atoms in the structure (Fig. 8) and the size of gaseous MeCl_x molecules penetrating through the film. By replacing chlorine with other halogens (F, Br or I) or supercritical water we gain additional control over the porous structure of the

film. Thus, it should be possible to control the pore size by selecting an appropriate gas/carbide couple.

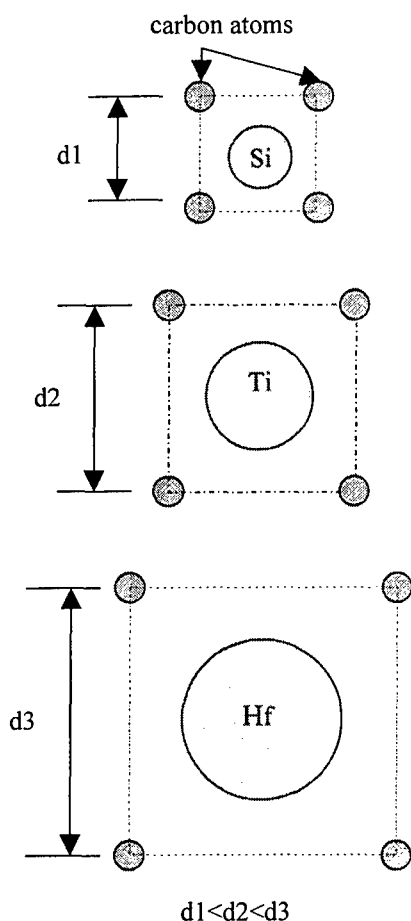


Figure 8. Structural templating of nanoporous carbon films.

approach has been demonstrated using SiC as an example. Supercritical water and chlorine were used for leaching a variety of SiC materials.

It has been shown that hydrothermal leaching produces smooth and uniform carbon films on SiC. Similar coatings have been obtained through the chlorination of SiC. Thermodynamic simulation shows that the suggested method can be applied to a variety of carbides, and other halogens can be used.

It allows us to solve the problems of uniformity and adherence of coatings, as well as avoid the bridging of filaments and/or particles. The principal difference between the

Differences in the composition and structure of carbide materials determine the differences in the reaction kinetics in different environments and structure of the coating. In general, the hydrothermal method worked better for polymer derived fibers. Extraction of silicon by chlorine was more efficient for CVD fibers and monolithic ceramics.

Synthesis of carbon coatings by leaching carbides is potentially an inexpensive technology because:

- The process is conducted at moderate or ambient pressures;
- It does not require plasma or other high-energy sources;
- The process can be scaled up to virtually any volume.

This is a more versatile process than CVD or PVD synthesis because:

- Almost any possible carbon structure can be obtained;
- Fibers, powders, whiskers and platelets, as well as complex shapes can be coated.

4. Conclusions

A new approach to the synthesis of carbon coatings on the surface of carbides has been developed. It is based on the idea of extracting metal atoms from the surface layer of carbides and subsequent conversion of the carbide surface into carbon. This

described method and other approaches is that the coating is not deposited on the surface of the carbide; rather the carbide surface is converted into carbon. This method can provide a simple and inexpensive route to carbon coatings (thickness from 1 nm to 100 μm) for a wide range of applications. Depending on the carbide substrate and the experimental conditions, dense or porous carbon coatings with a varying sp^2/sp^3 carbon ratio can be produced.

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